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Circular No. 12.

United States Department of Agriculture,

BUREAU OF CHEMISTRY,

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METHODS FOR THE INVESTIGATION OF CANCELING INKS AND OTHER STAMPING INKS.

The following methods have been devised for the purpose of ascertaining the suitability of canceling inks for the use of the Post-Office Department. Many of these methods will be found of assistance in passing upon the quality of stamping inks for miscellaneous uses.

It is important that the ink used by the Post-Office Department for postmarking possess in the highest possible degree certain properties. The ink, first of all, must produce an indelible cancellation; that is, it must be relatively indelible as compared with the ink used for printing the postage stamps. The postmark made with the ink must dry quickly in order that the mail matter may be handled immediately without any blurring or smearing of the postmark. Both this property and the property of the indelibility involve the question of the rate at which the ink penetrates or is absorbed by the fiber of the paper. A satisfactory ink does not harden or form a crust on the ink pad on exposure to the air. There must be no deposition of solid matter on the bottom of the vessel in which the ink is stored, and the pigments, on which the indelibility of the ink depends, if insoluble, must not settle out in such a way as to make it possible to pour off from the top of the container a portion of the ink which contains little or none of the insoluble pigment or pigments. The following methods have been found of value for the purpose of ascertaining the quality of a given sample of ink as well as the appropriateness of certain materials used for the manufacture of canceling inks:

I.—METHODS FOR THE INVESTIGATION OF INKS MADE WITH AN OIL BASE.

1. Preparation and Care of the Sample.

Since canceling inks contain more or less insoluble and volatile matter, special attention must be given to the preparation and care of the sample. It must be carefully mixed by shaking before each portion is removed for analysis, and the container must be left open no more than is absolutely necessary for the removal of portions of the ink.

2. Determination of Matter Volatile at Ordinary Temperatures.

Place a carefully weighed quantity (between 5 and 5.2 grams) of the ink in a flat-bottomed aluminum dish 102 mm (4 inches) in diameter. Distribute the ink com-

pletely over the surface of the bottom of the dish by gently tilting the same. This quantity of ink should be sufficient to completely cover the bottom of the dish. Place the dish on a horizontal shelf or table where air will have free access to it and where it will be screened in such a way that no dust can fall into it.

Reweigh the dish at the end of 18 hours, 24 hours, 3 days, 4 days, 5 days, 6 days, 7 days, 14 days, 21 days, and 28 days. Calculate the total percentage loss of weight at the end of each period of drying. The loss of weight should be gradual and should not exceed 15 per cent during the first 7 days, nor 25 per cent during 28 days. This test shows the absence of highly volatile ingredients and the absence of an excess of matter volatile at the ordinary room temperatures. The constituents of a canceling ink should be such that the volatile matter will not exceed the above limits when the ink is exposed under the conditions named to a summer temperature of 80° F. and upward.

3. Determination of Relative Penetrating Power

(1) *Apparatus.*

(*a*) Homeopathic shell vials about 8 cm long and 2 to 2.5 cm in diameter.

(*b*) Strips of white blotting paper, which for a given series of determinations should be cut from the same sheet and of exactly the same dimensions. A convenient size is 12 mm wide and 25 cm long.

(*c*) A pair of dividers with arms 15 cm long or longer.

(*d*) A millimeter rule.

(2) *Determination.*

Place approximately 5 cc of the ink or other material to be tested in one of the "shell vials" described above, and if several samples are to be tested arrange the vials in a row. Place 5 cc portions of distilled water in each of two of the vials, and put one of the vials containing water at each end of the row of vials containing samples to be tested. Insert one of the strips of blotting paper into each of the vials as quickly as practicable, proceeding from left to right. Record the time when the paper was placed in the left-hand vial containing water, and also the time when the paper was placed in the right-hand vial containing water. The vials should support the strips of blotting paper in a nearly upright position. The liquids gradually ascend the strips by capillarity; the strips, however, should be in such a position that the liquid does not ascend by capillarity between the edges of the strips and the sides of the vessels.

At the expiration of fifteen minutes from the time the strip of paper was placed in the left-hand vial of water begin measuring the heights to which the liquids have ascended the strips of paper, measuring this height by use of the dividers from the bottom of the meniscus of the liquid in the vial to the top of the wet portion of each strip of blotting paper. Measure the distance which the points of the dividers are separated by means of the millimeter rule, and record the result. The operations should be performed as rapidly as practicable, beginning with the left-hand vial and proceeding to each vial successively to the right. At the expiration of a second period of fifteen minutes or half hour repeat the measurements.

After all of the measurements have been recorded reduce the results to the terms of the penetrating power of distilled water, taking the penetrating power of distilled water as 100. This is accomplished by dividing each result by the result obtained for the distilled water contained in the left-hand vial and multiplying the quotient by 100. If the result obtained with the distilled water contained in the right-hand vial differs greatly from the result of the distilled water contained in the left-hand vial, the number of samples included in the test has been too great and the work should be repeated, including one-half or one-third the number of samples in each

series of tests. This method gives good comparative results, and has been applied not only to canceling and other stamping inks, but to the liquids used for the manufacture of these inks.

In observing the penetrating power of a given sample of ink it is important to remember that the value of a canceling or stamping ink depends upon its power to penetrate the paper during the first minute or fraction of a minute following its application to the paper. It is well, however, to keep the tests under observation for several hours, as information can thus be obtained in regard to the extent to which the coloring matter contained in the ink follows the liquid base of the ink as it passes through the paper. In some cases the coloring matters keep pace with the liquid portions of the ink; in others an uncolored band at the top of the portion of the paper which is wet with the ink shows that the coloring matter does not proceed through the paper as rapidly as the base of the ink. This may or may not be an undesirable result. If the colorless band is due to a difference in the rate of penetration, it is undesirable. If it shows that the dye contained in the ink has an affinity for the fibers of the paper, it is evidence of a valuable quality.

Additional information can be obtained from the penetration test by removing the strips of paper from the vials, cutting off the part of the paper which has actually been immersed in the ink, and treating the upper part successively with petroleum, ether, alcohol, and other solvents for removal of the constituents of the ink soluble in these liquids. The extent to which the dye or dyes contained in the ink resist the action of these solvents and the extent to which the lampblack has passed up the strip of blotting paper are indices of the quality of the ink.

4. Sedimentation Test.

(1) *Apparatus.*

(*a*) Glass-stoppered cylinders, graduated for 200 cc and fractions thereof. In order that comparative results may be obtained, cylinders have been adopted for this work for which the distance between the bottom and the 200 cc mark is approximately 25 cm. It should not be less than 24 cm, nor exceed 26 cm.

(*b*) A rubber stopper of the proper size to fit the mouths of the cylinders and provided with a blow tube and delivery tube, as shown in fig. 2, p. 36, of Prescott's Organic Analysis.

(2) *Determination.*

Place 25 cc of the ink to be tested in one of the 200 cc cylinders, and gradually add to it petroleum ether (boiling point, 50–60°), agitating the contents of the cylinder from time to time, in order to keep the ink thoroughly mixed with the petroleum ether. When the volume has been brought to about 180 cc, rinse off the stopper and the upper part of the cylinder, and bring the volume to exactly 200 cc with petroleum ether, being careful to leave little or no insoluble matter above the 200 cc graduation mark. Allow the cylinder to stand for a number of days, and record from time to time the position of the top of the layer of sediment which collects in the bottom of the cylinder.

After the settling of the top of the sediment has entirely ceased the volume of the sediment should equal or exceed 25 cc, the volume of ink taken for the test.

In the case of some inks, the supernatant liquid above the sediment is of such a dark color that there is difficulty in locating the top of the sediment, even when the cylinder is carefully inspected by light reflected at various angles. In this case, place the cork with blow tube and delivery tube in the top of the cylinder, and by careful manipulation remove the supernatant liquid down to, or nearly to, the top of the sediment. Fill the cylinder again with petroleum ether as described above, and allow the insoluble matter to separate again. This process should be repeated until

it is possible to obtain an accurate reading of the position of the top of the sediment after the insoluble matter has finally come to rest.

The 25 cc portion of ink used for this test may be obtained by measuring it in the cylinder, or the specific gravity of the ink may be determined and a portion equivalent to 25 cc obtained by weighing.

5. Determination of Lampblack and Other Constituents.

(a) method by use of the soxhlet extraction apparatus.

(1) *Apparatus.*

(*a*) Schleicher and Schüll paper thimbles for the Soxhlet extraction apparatus, 30 by 77 mm in size and 33 by 80 mm in size.

(*b*) Extraction apparatus of Soxhlet or other convenient form, of such size as will admit of the use of S. & S. thimbles 33 by 80 mm.

(*c*) Fat-free cotton.

(*d*) Fat-free filter papers, S. & S. No. 589, Blue Ribbon, 12½ cm in diameter.

(*e*) Glass-stoppered weighing tubes sufficiently large to contain an S. & S. thimble 33 by 80 mm in size, and one or two pieces of the filter paper described under (*d*).

(2) *Matter soluble in petroleum ether, oil, etc.*

Prepare one of the larger 33 by 80 mm thimbles for each determination. With a sharp-pointed instrument make two holes on opposite sides of the thimble near the top, in order that a platinum or copper wire may be passed through it for the purpose of supporting the thimble during the filtration about to be described. Fill the thimble about half full with fat-free cotton, which should be packed tightly. Prepare another roll of cotton of such a size as will a little more than fill the upper half of the thimble and which is rolled in such a way that it can be removed from and returned to the thimble without loss of the fibers of the cotton.

Place the thimble thus prepared in the weighing tube and dry the whole to constant weight in a water oven or other proper drying apparatus.

Place an accurately weighed portion of the ink (approximately 5 grams) in a 300 cc beaker and dilute the same with petroleum ether (boiling point 40°–50°) to a volume of 250 cc. Stir thoroughly and allow to stand for a half hour or more. Remove the dried and weighed thimble from its weighing tube and remove from the thimble the upper plug of cotton. Pass a platinum or copper wire through the perforations near the top of the thimble and suspend the latter in the neck of a large flask in such a way that the flask can be covered with a watch glass.

Decant the diluted ink onto the cotton contained in the lower part of the thimble; add the ink solution a little at a time, being careful not to fill the thimble more than about half full. Keep the flask containing the thimble covered with a watch glass as much of the time as practicable to avoid the condensation of moisture on the thimble. Rinse the insoluble residue into the thimble with the aid of some petroleum ether contained in a wash bottle. Use, if necessary, small fragments of the fat-free filter paper which was weighed along with the thimble, for the purpose of removing insoluble matter from the beaker. It is generally possible to remove insoluble matter from the beaker so thoroughly that it is not necessary to weigh the beaker in order to ascertain the amount of residue left therein. If these operations have been successfully performed, no lampblack will pass through the thimble. The filtrate should, however, be saved, in order that the analyst may note whether any lampblack has passed through the thimble. This can best be ascertained after the filtrate has been allowed to stand at rest for several hours. In case lampblack or other insoluble matter of the ink does pass through the thimble, two thimbles should be employed, one of the 30 by 77 mm being slipped inside of one of the 33 by 80 mm size. The space between the two should be filled with fat-free cotton.

Place the thimble in the Soxhlet extraction apparatus and extract with petroleum ether (boiling point 40°–50°) until the oil is entirely removed from the ink. It is not possible in most cases to rely upon the color of the extract, as most of the dyes used in these inks are slightly soluble in petroleum ether, and this method is therefore defective to the extent of that solubility.

After the extraction apparatus has been in operation for six to eight hours, 25 cc of the extract should be evaporated in a clean vessel and the residue inspected to determine whether the oil is completely removed from the ink. When this is the case, remove the thimble from the apparatus, place it in a beaker, and allow to stand in a moderately warm place until the ether has evaporated or drained from the thimble. When this has taken place, put the thimble and its weighing tube in the water oven and dry to constant weight.

The loss of weight of the portion of ink taken is to be calculated as oil and other constituents forming the base of the ink. The residue in the thimble (and possibly in the beaker also) consists of the greater part of the coal-tar dye and all of the lampblack, together with any other constituents of the ink insoluble in petroleum ether.

(3) *Matter soluble in alcohol, coal-tar dye, etc.*

After the weight of the petroleum ether insoluble residue has been obtained, return the thimble to the extraction apparatus and extract with 95 per cent alcohol, the extraction being continued until the extract is no longer colored. Remove the thimble from the extraction apparatus and dry to constant weight. After the alcohol extraction the thimble can be placed directly in the water oven, after it has been allowed to drain thoroughly. In the case of the petroleum ether extraction, however, a part of the contents of the thimble are likely to be thrown out if it is heated too rapidly at the beginning. The difference between the weight of matter insoluble in petroleum ether and the weight of matter insoluble in both petroleum ether and alcohol may generally be considered to consist of a coal-tar dye, and the percentage calculated therefrom. The percentage thus obtained will be more or less too small, depending upon the solubility of the dyes in petroleum ether. A qualitative examination of the alcohol extract should be made, to make certain that it contains no considerable quantity of any substances other than coal-tar dyes.

(4) *Matter insoluble in alcohol, lampblack, etc.*

From the residue insoluble in alcohol the percentage of lampblack may be obtained. The matter insoluble in alcohol must, however, be examined qualitatively to make certain that other substances are not present in quantities sufficient to materially affect the results.

(B) METHOD BY USE OF WEIGHED FILTER PAPERS.

If a Soxhlet extraction apparatus or its equivalent is not available, the analysis of a canceling or stamping ink can be made by a scheme similar to the one just outlined, using weighed filter papers instead of S. & S. thimbles.

When this is done, three or four filter papers (S. & S. No. 589, Blue Ribbon, have been found satisfactory for the work) should be placed in each weighing tube and dried to constant weight. Some inks may require the use of double filters in order to obtain clear filtrates. The extra filter papers will be found essential in removing insoluble matter from the beaker in which the ink is weighed and diluted, from the stirring rod, etc.

6. DETERMINATION OF ASH.

The lampblacks prepared for the manufacture of canceling ink yield less than 0.5 of 1 per cent of ash when burned, and the coal tar-dyes employed should contain no

mineral matter other than that which is an essential part of the molecules of the substances to which the tinctorial power of these dyes is due.

For the determination of the ash, place 2 to 3 grams of the ink in a porcelain dish, which must be of such size as to avoid loss of ink due to the foaming which is likely to attend the beginning of the incineration. Heat the dishes thus charged in a muffle at a low, red heat until all organic matter and uncombined carbon have been burned. Cool and weigh.

If an excessive percentage of ash is found, the percentage of mineral matter contained in the alcoholic extract should be determined by incineration of the residue obtained after evaporation of this extract. If either of the total ash or the ash of the alcoholic extract is high, a qualitative examination should be made.

7. Resistance of Pigments and Dyes to Light and Reagents.

It is necessary in the case of canceling inks, and important, if not necessary, in the case of many stamping inks, that the pigments and dyes employed in their manufacture be as resistant as possible to means which may be employed for the erasure of marks made by them on paper. Under this heading may be mentioned also the importance of the use of dyes which possess considerable affinity for vegetable fibers. It is not practicable to enumerate the agents which should be employed in experiments to ascertain the resistance of a given dye to erasure, as light, heat, and all of the solvents and reagents known to the chemist are available for the use of persons who might desire them for use in assisting them in making fraudulent erasures.

For the purpose of canceling postage stamps, it is necessary that the canceling marks be substantially indelible, because the inks used in printing many of the stamps are very resistant. Stamping inks used for other purposes, however, do not require absolute indelibility.

II.—METHODS FOR THE INVESTIGATION OF RUBBER-STAMP INKS.

1. Preparation and Care of Sample.

The precautions given in regard to the care of samples of inks made with an oil base should be observed.

2. Change of Weight on Exposure to Air.

This determination should be conducted in the manner described for the determination of volatile matter in inks made with an oil base. Rubber-stamp inks, however, gain or lose in weight according to the constituents used in their manufacture and according to atmospheric conditions. A rubber-stamp ink should not, however, undergo very much greater changes in weight when exposed to the air under given conditions than diluted glycerin containing 75 per cent of glycerin and 25 per cent of water.

3. Penetrating Power.

This test should be conducted in the manner described above for inks made with an oil base.

4. Sedimentation Test.

This test should be conducted as described for inks made with an oil base, with the exception that the 25 cc portions of ink should be diluted with water instead of petroleum ether.

5. Determination of Lampblack and Other Constituents.

A scheme of analysis similar to that described above for inks made with an oil base should be employed. Some experiments will be necessary in most cases to

ascertain the proper solvent to be used in the case of each sample of ink to be examined. Alcohol, however, will generally be found to be satisfactory for rubber-stamp inks.

The amount of coloring matter contained in the alcoholic extract can be ascertained by spectro-colorimetric or by comparative dyeing tests. Both of these methods involve the previous identification of the dyes present by qualitative tests.

For the quantitative determination of glycerin in canceling inks a modification of a method for the determination of glycerin in wines may be employed.[a] The acetylization method may also be used.[b]

6. Resistance to Light and Reagents.

The remarks made above in regard to the investigation of the resistance of cancellations made with oil inks apply in general to canceling and other inks for use with rubber stamps.

III.—METHODS FOR THE INVESTIGATION OF MATERIALS USED FOR THE MANUFACTURE OF CANCELING AND OTHER STAMPING INKS.

1. Volatility and Penetrating Power.

The methods which have been described above will be found useful in determining the suitability of liquids for use as bases or constituents of bases of canceling and other stamping inks.

2. Sedimentation Test.

A modification of the sedimentation test described above may be employed with good results for the purpose of ascertaining the suitability of lampblack and other pigments for use in the manufacture of canceling and other stamping inks. The results, of course, are mainly of value for purposes of comparison.

The conditions of the test may be modified to suit the purposes of the investigation and the character of the materials to be compared. The writer has obtained good results in the comparison of lampblacks and other blacks rich in uncombined carbon by the following method, which was so planned that the results might be applied to stamping inks made with either a water-soluble base or with an oil base:

Mix 0.5 gram of the black to be tested in a mortar with dilute glycerin (87.5 cc of glycerin diluted with water to 1 liter). Rinse the mixture into a 100 cc Nessler cylinder and dilute to the 100 cc mark, using the same dilute glycerin. After having prepared a series of tubes, each containing a portion of one of the blacks to be tested, close each tube with a cork and shake thoroughly each tube successively, performing the operation as quickly as possible in order that the time of settling may be approximately the same in the case of each sample. Allow the cylinders to stand at rest in a place free from jar, and record from time to time the height of the sediment formed by the deposition of the blacks. When submitted to this test, a black which is suitable for the manufacture of a canceling or stamping ink should occupy a volume of not less than 25 cc when the sediment has stopped settling.

3. Ash, etc.

Blacks, dyes, and other substances used for the manufacture of canceling and other stamping inks should be carefully examined to insure the absence of considerable

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[a] This method is described on page 63 of Bulletin 46 of the Bureau of Chemistry of the Department of Agriculture, which contains the methods of analysis of the Association of Official Agricultural Chemists.

[b] See Benedikt and Cantor, Zeitschr. angew. Chem., 1888, 460, and Vaubel, "Die physikalischen und chemischen Methoden der quantitativen Bestimmung organischer Verbindungem," II Band, 134-140.

percentages of substances which are not essential to the production of an ink of good quality. It can generally be assumed that the presence of considerable quantities of any substance which does not actually contribute to the desirable qualities of the ink will detract therefrom.

Black pigments rich in carbon of high specific gravity due to the presence of a large percentage of ash are highly unsuitable for the manufacture of stamping inks. Only the concentrated brands of coal-tar dyes should be used, unless the substances with which the less concentrated are diluted have been found to actually contribute to the working qualities of the ink to be produced.

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Approved:
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Washington, D. C., *January 29, 1903.*

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